

Regioselective ring opening of 2,2-dicyanooxiranes by 1,3-dinucleophiles in the presence of Lewis acids such as bismuth(III) nitrate pentahydrate $[\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}]$ and zirconium(IV) chloride (ZrCl_4)

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Abstract Bismuth(III) nitrate pentahydrate $[\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}]$ or zirconium(IV) chloride (ZrCl_4) has been shown to catalyze nucleophilic ring opening of 2,2-dicyanooxiranes along with ring closure by 1,3-dinucleophiles such as 1*H*-1,3-benzimidazole-2-thiol, 5-phenyl-4*H*-1,2,4-triazole-3-thiol, and thioureas. These reactions led to efficient synthesis of heterocyclic compounds condensed with benzimidazole or triazole derivatives. The used catalysts are inexpensive, highly efficient, and reusable for opening of epoxides with 1,3-dinucleophiles at ambient temperature, with excellent regioselectivity.

Keywords Bismuth(III) nitrate pentahydrate $[\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}]$ · Zirconium(IV) chloride · 1*H*-1,3-Benzimidazole-2-thiol · 5-Phenyl-4*H*-1,2,4-triazole-3-thiol · Thioureas · 2,2-Dicyanooxiranes

Introduction

2,2-Dicyanooxiranes and their α -haloketone derivatives are known as very effective bielelectrophile reagents for synthesis of a large variety of heterocyclic compounds such as thiazoles [1], dithioles [2], imidazoles [3], 1,3-oxathioles [4], and condensed imidazolo and thiazolo derivatives [5]. In general, nucleophilic reagents can react with these compounds regioselectively: they can attack the oxirane ring, cyano functional group to give either ring-opened products, new functionalized oxiranes or different heterocycles. Epoxide ring opening with nucleophilic agents is an important step in preparation of 1,2-disubstituted products [6]. Heating epoxides in the presence of nucleophiles, which would occur with poorly nucleophilic addition, suffers from lack of appreciable regioselectivity [6]. The requirement for high

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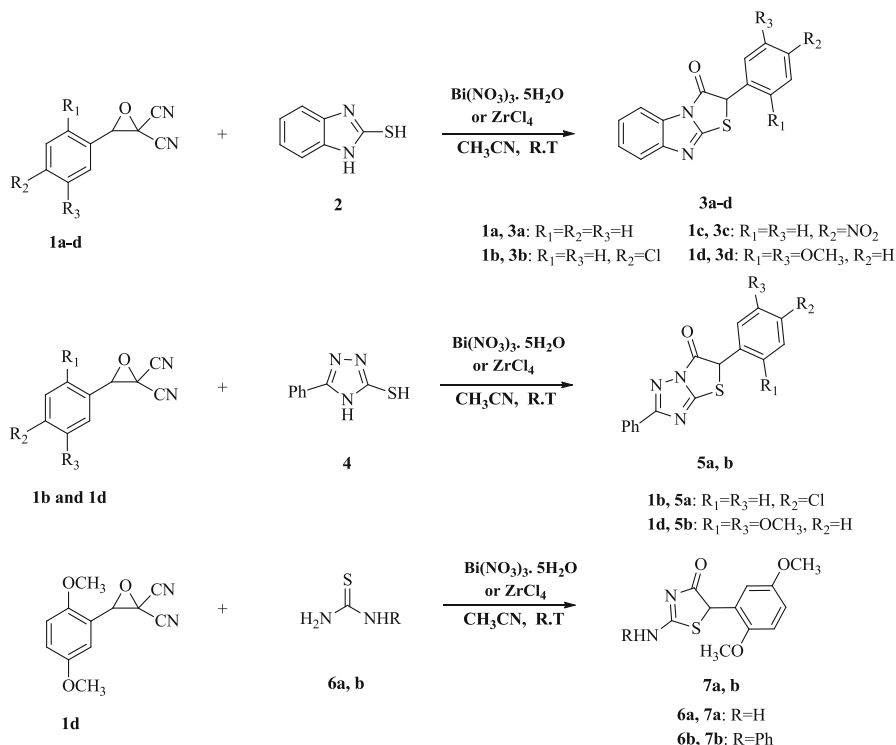
temperature in epoxides sensitive to this condition led to the necessity for activation of the epoxide rings to increase their susceptibility to nucleophilic attack. The various methodologies developed for this purpose include the use of Lewis acid catalysts such as alumina [7], metal triflates [8], transition-metal halides [9], alkali-metal perchlorates [10], silica under high pressure [11], and montmorillonite clay under microwave irradiation [12]. The search for new and efficient Lewis acid catalysts for various useful organic transformations is one of the most important, interesting, and challenging research topics in catalytic synthesis. On the other hand, in recent years, economically affordable ecofriendly catalysts have received greater acceptance for use in organic reactions. In this respect, bismuth(III) and zirconium(IV) derivatives are known as Lewis acid catalysts in various organic transformations involving carbon–carbon bond formation, protection-deprotection chemistry, and conversion of epoxides into *vic*-acylamino hydroxy compounds [13–16]. Since zirconium, in its normal quadrivalent state, displays no redox properties but can attain a maximum covalency up to eight and displays low toxicity [16], Zr(IV) compounds should be ideal for catalytic applications. Coordination of Bi^{3+} with the epoxide oxygen renders the epoxide susceptible to nucleophilic attack by nucleophilic reagents. Considering the widespread applications of 2,2-dicyanooxiranes in synthesis of a large variety of heterocyclic compounds and their sensitivity to high temperature, we planned to employ bismuth(III) nitrate pentahydrate and zirconium(IV) chloride as Lewis acid catalysts to evaluate their catalytic efficiency in carrying out ring-opening reactions of these epoxides with 1,3-dinucleophiles.

Results and discussion

We investigated ring opening and condensation reaction of 2,2-dicyanooxiranes (**1a–1d**) with 1,3-dinucleophiles such as 1*H*-1,3-benzimidazole-2-thiol (**2**), 5-phenyl-4*H*-1,2,4-triazole-3-thiol (**4**), and thioureas (**6a**, **6b**) in different conditions at ambient temperature (Scheme 1). Lewis acid catalysts, namely bismuth(III) nitrate pentahydrate and zirconium(IV) chloride, were used for activation of the epoxide rings, rendering them more susceptible to nucleophilic attack under milder conditions. Selective formation of the regioselective products **3**, **5**, and **7** arising from nucleophilic attack at the benzylic carbon (C_β) of 2,2-dicyanooxiranes (**1a–1d**) was observed in the course of the reactions with 1,3-dinucleophiles **2**, **4**, and **6**.

Reactions of 2,2-dicyanooxiranes with 1,3-dinucleophiles occur at ambient temperature in the absence of catalyst in long experimental times [17–19]. These epoxides are sensitive to high temperature; therefore, we planned to employ Lewis acid catalysts bismuth(III) nitrate pentahydrate and zirconium(IV) chloride to decrease the activation energy of the ring-opening reaction of epoxides with 1,3-dinucleophiles (Table 1).

To determine standard operating conditions for these reactions, we used some polar and nonpolar solvents in the reaction of 3-phenyloxirane-2,2-dicarbonitrile (**1a**) and 1*H*-benzo[*d*]imidazole-2-thiol (**2**) in the presence of Lewis acid catalysts bismuth(III) nitrate pentahydrate and zirconium(IV) chloride as model reactions to



Scheme 1 Condensation reaction of 2,2-dicyanooxiranes (**1a–1d**) with 1,3-dinucleophiles such as 1*H*-1,3-benzimidazole-2-thiol (**2**), 5-phenyl-4*H*-1,2,4-triazole-3-thiol (**4**), and thioureas (**6a**, **6b**)

Table 1 Reaction of 1,3-dinucleophiles (**2**, **4**, **6a**, **6b**) with 2,2-dicyanooxiranes (**1a–1d**) for synthesis of **3a–3d**, **5a**, **5b**, **7a**, and **7b** in the presence of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (5 mol.%) and ZrCl_4 (10 mol.%)

Compd.	Oxirane	Dinuc.	Without catalyst		$\text{Bi}(\text{NO}_3)_3$ (5 mol.%)		ZrCl_4 (10 mol.%)	
			Time (h)	Yield (%)	Time (min)	Yield (%)	Time (min)	Yield (%)
3a	1a	2	7	90	40	90	30	92
3b	1b	2	7	93	35	92	25	94
3c	1c	2	7	94	35	95	25	95
3d	1d	2	7	90	40	93	35	94
5a	1b	4	7	90	30	92	25	92
5b	1d	4	7	94	35	94	30	94
7a	1d	6a	24	68	70	83	60	85
7b	1d	6b	24	70	75	88	70	90

investigate the effects of solvent for preparing compound **3a**. In each case, the substrates were mixed together with 10 mol.% of these catalysts agitated with 10 mL solvent at room temperature. The results are presented in Table 2. It is

noteworthy that polar solvents such as acetonitrile afforded better yields than nonpolar solvents.

We also optimized the quantity of catalysts. The best results were obtained when the reactions were carried out in the presence of 5 or 10 mol.% bismuth(III) nitrate pentahydrate and zirconium(IV) chloride, respectively. The results are presented in Table 3.

We also attempted to reuse the catalysts by a variety of methods (Table 4). Direct reuse of the catalysts (Table 4, entry 2, 6) led to a greater than 15 % decrease in activity, while washing with dichloromethane and ethylacetate prior to reuse also resulted in lower conversions (Table 4, entry 3, 4, 7, 8). This phenomenon probably arose because the reactant and product were not completely desorbed from the catalyst, and therefore the active sites were blocked.

Using this protocol (Scheme 1), we investigated reactions of 2,2-dicyanooxiranes **1**, which have three electron-deficient centers, with 1,3-dinucleophiles for synthesis of heterocyclic compounds in the presence of Lewis acid catalysts $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (5 mol.%) and ZrCl_4 (10 mol.%). In these reactions, the 1,3-dinucleophiles act

Table 2 Solvent effects on ring-opening reaction of epoxide **1a** with 1*H*-benzo[d]imidazole-2-thiol (**2**)

Entry	Solvent	Catalyst	Time (min)	Yield (%)
1	Toluene	$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$	80	75
2	Toluene	ZrCl_4	70	78
3	THF	$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$	48	87
4	THF	ZrCl_4	37	89
5	CH_3CN	$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$	40	90
6	CH_3CN	ZrCl_4	30	92
8	Ethanol	$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$	45	88
9	Ethanol	ZrCl_4	35	91

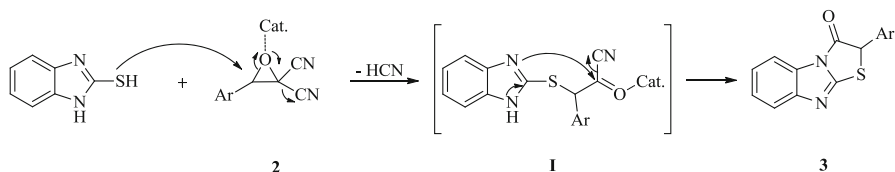
THF tetrahydrofuran

Table 3 Optimized quantity of catalysts for ring-opening reaction of epoxide **1a** in synthesis of compound **3a**

Entry	Catalyst	Mol.% catalyst	Time (min)	Yield (%)
1	$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$	3	50	85
2	ZrCl_4	5	38	88
3	$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$	4	45	87
4	ZrCl_4	7.5	35	89
5	$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$	5	40	90
6	ZrCl_4	10	30	92
7	$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$	6	40	90
8	ZrCl_4	12.5	30	92
9	$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$	7	40	90
10	ZrCl_4	15	30	92

Table 4 Reusability of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and ZrCl_4 in ring-opening reaction of epoxide **1a** for synthesis of compound **3a**

Entry	Catalyst	Time (min)	Yield (%)
1	$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (1st use)	40	90
2	$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}^{\text{a}}$ (2nd use)	70	75
3	$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}^{\text{b}}$ (2nd use)	55	83
4	$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}^{\text{c}}$ (2nd use)	55	81
5	ZrCl_4 (1st use)	30	92
6	ZrCl_4^{a} (2nd use)	55	78
7	ZrCl_4^{b} (2nd use)	40	85
8	ZrCl_4^{c} (2nd use)	40	84

^a Direct reuse of catalysts^b $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and ZrCl_4 were washed with dichloromethane^c $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and ZrCl_4 were washed with ethylacetate**Scheme 2** A reasonable mechanism for formation of product **3**

regioselectively on C_β and C_α of 2,2-dicyanooxiranes **1**, which have three electron-deficient centers. These processes are highly regioselective, with the products resulting from initial attack of the nucleophilic sulfur atom of compounds **2**, **4** or **6** on C_β of 2,2-dicyanooxiranes **1** followed by ring opening. The intermediate **I** was formed by loss of cyano group. The last step is intramolecular nucleophilic addition of nitrogen on carbonyl group of intermediate **I**, followed by elimination of HCN to form a single product. Coordination of the Lewis acids with the epoxide and carbonyl group oxygen increases the polarity of the C–O bond and makes the adjacent carbons more susceptible to nucleophilic attack (Scheme 2).

Conclusions

Bismuth(III) nitrate pentahydrate and zirconium(IV) chloride are known as effective Lewis acid catalysts for synthesis of heterocyclic compounds which condensed [1,3]thiazole with benzimidazole, triazole or thiazolinone derivatives via nucleophilic reaction of 1,3-dinucleophiles with 2,2-dicyanooxiranes at ambient temperature. These catalysts show an environmentally friendly character and are inexpensive and easily obtained. Moreover, the procedure offers several advantages including high yield, operational simplicity, clean reaction conditions, and short

reaction time, making it a useful and attractive process for synthesis of these compounds.

Experimental

General procedures

Melting points were measured on an Electrothermal Engineering Ltd. apparatus and are uncorrected. Infrared (IR) spectra were measured on a Mattson 1000 FT-IR spectrometer. Proton and carbon nuclear magnetic resonance (NMR) spectra were recorded with a Bruker DRX-400 AVANCE spectrometer at 400 and 100 MHz, respectively. Mass spectra were recorded on a MS-QP2000A Shimadzu mass spectrometer operating at an ionization potential of 70 eV. Elemental analyses were performed using a Heraeus CHN-O-Rapid analyzer. 2,2-Dicyanooxiranes **1a–1d** were prepared according to a literature procedure [18].

*Procedure for preparation of 2-arylidene-[1,3]thiazolo[3,2-*a*]benzimidazol-3(2H)-ones (3a–3d), 5-substituted thiazolo[3,2-*b*][1,2,4]triazol-6-ones (5a, 5b), and thiazolinones (7a, 7b)*

A mixture of 2,2-dicyanooxiranes **1a–1d** (2 mmol), 1H-benzo[*d*]imidazole-2-thiol **2** or 5-mercapto-3-phenyl-*s*-triazole **4** or thioureas (**6a**, **6b**) (2 mmol), and ZrCl₄ (10 mol.%) or Bi(NO₃)₃·5H₂O (5 mol.%) in CH₃CN (20 mL) was stirred for the appropriate time (Table 1), the progress of the reaction being monitored by thin-layer chromatography (TLC) using hexane/ethylacetate as eluent. When the reaction was completed as indicated by TLC, the crude product **3a–3d**, **5a**, **5b**, **7a**, and **7b** was precipitated from the reaction mixture, and the solid was filtered and recrystallized with hexane/ethylacetate to get pure product.

2-Phenyl[1,3]thiazolo[3,2-*a*]benzimidazol-3(2H)-one (3a) White crystals; m.p. 190–192 °C. IR (KBr, $\nu_{\text{max}}/\text{cm}^{-1}$): 1,742 (C=O), 1,603 (C=N). ¹H NMR (400 MHz, DMSO-*d*₆): 8.81 (d, 1H, ³J_{H-H} = 8 Hz, CH), 7.71 (d, 1H, ³J_{H-H} = 8 Hz, CH), 7.67–7.39 (m, 7H, Ar), 6.40 (s, 1H). ¹³C NMR (100 MHz, DMSO-*d*₆): 153.84 (C=O), 144.75 (C=N), 142.92, 133.21, 132.69, 132.38, 129.45, 129.04, 128.93, 124.63, 122.87, 117.76, 50.10 (C₂). MS (*m/z*): 266 (M⁺(98), 237 (80), 205 (20), 150 (15), 121 (100), 90 (78), 77 (40). Anal. calcd. for C₁₅H₁₀N₂OS: C, 67.65; H, 3.78; N, 10.52 %. Found: C, 67.42; H, 3.66; N, 10.18 %.

2-(4-Chlorophenyl)[1,3]thiazolo[3,2-*a*]benzimidazol-3(2H)-one (3b) White crystals; m.p. 136–139 °C. IR (KBr, $\nu_{\text{max}}/\text{cm}^{-1}$): 1,726 (C=O), 1,609 (C=N). ¹H NMR (400 MHz, DMSO-*d*₆): 7.87 (d, 1H, ³J_{H-H} = 8 Hz, CH), 7.66 (d, 1H, ³J_{H-H} = 8 Hz, CH), 7.62 (d, 2H, ³J_{H-H} = 8.8 Hz, CH), 7.50 (d, 2H, ³J_{H-H} = 8.8 Hz, CH), 7.42 (t, 1H, ³J_{H-H} = 8 Hz, CH), 7.35 (d, 1H, ³J_{H-H} = 8 Hz, CH), 6.32 (s, 1H). ¹³C NMR (100 MHz, DMSO-*d*₆): 166.83 (C=O), 156.88 (C=N),

149.42, 133.61, 133.44, 131.17, 128.72, 128.02, 125.77, 123.74, 123.35, 118.70, 67.32 (C₂). MS (*m/z*): 300 (M⁺) (100), 27 (70), 237 (50), 156 (80), 124 (20), 89 (73), 63 (40). Anal. calcd. for C₁₅H₉ClN₂OS: C, 59.90; H, 3.02; N, 9.31 %. Found: C, 59.83; H, 2.88; N, 9.01 %.

2-(4-Nitrophenyl)[1,3]thiazolo[3,2-*a*]benzimidazol-3(2*H*)-one (3c) White crystals; m.p. 193–196 °C. IR (KBr, $\nu_{\text{max}}/\text{cm}^{-1}$): 1,750 (C=O), 1,609 (C=N). ¹H NMR (400 MHz, DMSO-*d*₆): 8.49 (d, 2H, ³J_{H-H} = 8 Hz, CH), 7.72 (d, 1H, ³J_{H-H} = 8 Hz, CH), 7.50–7.26 (m, 5H, Ar), 5.79 (s, 1H). ¹³C NMR (100 MHz, DMSO-*d*₆): 165.83 (C=O), 153.20 (C=N), 150.3, 145.4, 140.01, 138.5, 129.73, 126.56, 124.55, 124.49, 119.51, 128.9, 57.61 (C₂). MS (*m/z*): 311 (M⁺) (100), 282 (20), 265 (15), 236 (40), 167 (98), 151 (20), 145 (50), 121 (30), 109 (20), 90 (77), 77 (80), 63 (88). Anal. calcd. for C₁₅H₉N₃O₃S: C, 57.87; H, 2.91; N, 13.50 %. Found: C, 57.69; H, 2.85; N, 13.21 %.

2-(2,5-Dimethoxyphenyl)[1,3]thiazolo[3,2-*a*]benzimidazol-3(2*H*)-one (3d) Yellow crystals; m.p. 140–143 °C. IR (KBr, $\nu_{\text{max}}/\text{cm}^{-1}$): 1,748 (C=O), 1,611 (C=N). ¹H NMR (400 MHz, DMSO-*d*₆): 7.81 (d, 1H, ³J_{H-H} = 8 Hz, CH), 7.49 (d, 1H, ³J_{H-H} = 8 Hz, CH), 7.31–7.12 (m, 2H, CH), 7.05 (s, 1H, CH), 7.02 (d, 1H, ³J_{H-H} = 8 Hz, CH), 6.88 (d, 1H, ³J_{H-H} = 8 Hz, CH), 6.01 (s, 1H), 3.65, 3.48 (s, 6H, 2OCH₃). ¹³C NMR (100 MHz, DMSO-*d*₆): 167.91 (C=O), 154.70 (C=N), 152.59, 150.56, 126.40, 124.75, 124.38, 123.38, 119.61, 117.79, 116.30, 56.88, 56.09 (2OCH₃) 57.61 (C₂). MS (*m/z*): 326 (M⁺) (100), 311 (85), 267 (20), 178 (15), 163 (50), 149 (60), 135 (20), 121 (40), 107 (12), 91 (30), 77 (43), 63 (35). Anal. calcd. for C₁₇H₁₄N₂O₃S: C, 62.56; H, 4.32; N, 8.58 %. Found: C, 62.44; H, 4.28; N, 8.31 %.

5-(4-Chlorophenyl)-2-phenylthiazolo[3,2-*b*][1,2,4]triazol-6(5*H*)-one (5a) White crystals; m.p. 152–155 °C. IR (KBr, $\nu_{\text{max}}/\text{cm}^{-1}$): 1,744 (C=O), 1,692, 1,611 (C=N). ¹H NMR (400 MHz, DMSO-*d*₆): 8.13–8.11 (m, 2H, Ar), 7.64 (d, 2H, ³J_{H-H} = 8 Hz, CH), 7.57–7.53 (m, 3H, Ar), 7.50 (d, 2H, ³J_{H-H} = 8 Hz, CH), 6.41 (s, 1H). ¹³C NMR (100 MHz, DMSO-*d*₆): 169.73 (C=O), 165.03, 163.96 (C=N), 134.00, 132.56, 131.35, 131.27, 129.15, 129.04, 128.97, 126.90, 58.17 (C₅). MS (*m/z*): 327 (M⁺) (80), 301 (12), 281 (12), 264 (55), 177 (20), 152 (60), 125 (40), 103 (100), 89 (85), 77 (30). Anal. calcd. for C₁₆H₁₀ClN₃OS: C, 58.63; H, 3.07; N, 12.28 %. Found: C, 58.44; H, 2.98; N, 11.97 %.

5-(2,5-Dimethoxyphenyl)-2-phenylthiazolo[3,2-*b*][1,2,4]triazol-6(5*H*)-one (5b) Orange crystals; m.p. 204–206 °C. IR (KBr, $\nu_{\text{max}}/\text{cm}^{-1}$): 1,754 (C=O), 1,606 (C=N). ¹H NMR (400 MHz, DMSO-*d*₆): 8.13 (d, 2H, ³J_{H-H} = 8 Hz, CH), 7.70–7.66 (m, 3H, Ar), 7.20 (s, 1H, CH), 7.05–7.00 (m, 2H, CH), 6.31 (s, 1H), 3.76, 3.67 (s, 6H, 2OCH₃). ¹³C NMR (100 MHz, DMSO-*d*₆): 169.09 (C=O), 164.73, 164.32 (C=N), 153.08, 151.17, 131.19, 129.10, 129.05, 126.88, 122.58, 117.28, 115.78, 56.45, 55.84 (2OCH₃), 55.67 (C₅). MS (*m/z*): 353 (M⁺) (12), 294 (7), 178 (30), 163 (95), 147 (20), 135 (23), 121 (15), 103 (100), 92 (18), 77 (28). Anal. calcd. for C₁₈H₁₅N₃O₃S: C, 61.18; H, 4.28; N, 11.89 %. Found: C, 60.95; H, 4.15; N, 11.60 %.

2-Amino-5-(2,5-dimethoxyphenyl)thiazol-4(5H)-one (7a) Yellow crystals; m.p. 195–196 °C. IR (KBr, $\nu_{\text{max}}/\text{cm}^{-1}$): 3,316 (NH_2), 1,692 (C=O). ^1H NMR (400 MHz, DMSO-d_6): 8.92 (s, 2H, NH_2), 7.28 (d, 1H, $^3J_{\text{H-H}} = 8$ Hz, CH), 7.15 (d, 1H, $^3J_{\text{H-H}} = 8$ Hz, CH), 6.98 (s, 1H, CH), 5.91 (s, 1H, CH), 3.72, 3.65 (s, 6H, 2OCH_3). ^{13}C NMR (100 MHz, DMSO-d_6): 176.25 (C=O), 169.24 (C=N), 153.33, 150.28, 127.48, 116.15, 114.36, 113.56, 56.25, 55.68 (2OCH_3), 54.94 (C_5). MS (m/z): 252 (M^+) (16), 221 (15), 190 (38), 137 (58), 115 (100), 74 (25). Anal. calcd. for $\text{C}_{11}\text{H}_{12}\text{N}_2\text{O}_3\text{S}$: C, 52.37; H, 4.79; N, 11.10 %. Found: C, 52.18; H, 4.39; N, 10.98 %.

5-(2,5-Dimethoxyphenyl)-2-(phenylamino)thiazol-4(5H)-one (7b) White crystals; m.p. 218–220 °C. IR (KBr, $\nu_{\text{max}}/\text{cm}^{-1}$): 3,303 (NH), 1,702 (C=O). ^1H NMR (400 MHz, DMSO-d_6): 9.12 (s, 1H, NH), 7.38 (d, 1H, $^3J_{\text{H-H}} = 8$ Hz, CH), 7.27 (d, 1H, $^3J_{\text{H-H}} = 8$ Hz, CH), 7.23–7.02 (m, 5H, Ar), 6.89 (s, 1H, CH), 5.78 (s, 1H, CH), 3.76, 3.69 (s, 6H, 2OCH_3). ^{13}C NMR (100 MHz, DMSO-d_6): 173.63 (C=O), 168.23 (C=N), 153.03, 151.10, 134.32, 128.69, 128.45, 127.65, 124.85, 116.87, 114.16, 113.24, 56.45, 55.63 (2OCH_3), 54.86 (C_5). MS (m/z): 328 (M^+) (10), 297 (26), 266 (16), 251 (58), 191 (12), 189 (26), 137 (34), 77 (100). Anal. calcd. for $\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_3\text{S}$: C, 62.18; H, 4.91; N, 8.53 %. Found: C, 61.97; H, 4.48; N, 8.12 %.

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